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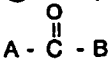
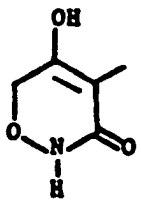
(54) Heterocyclic diones as pesticides and plant growth regulators.

(57) Compounds of the general formula I



wherein
A represents the group (i)



(i)

in which any free hydrogen may be replaced by an agriculturally acceptable substituent; and B represents an optionally substituted aryl or heteroaryl group are disclosed, as well as methods of producing such compounds, intermediates therefore, and their use as herbicides and acaricides.

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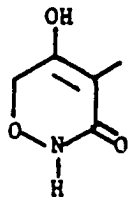
HETEROCYCLIC DIONES AS PESTICIDES AND PLANT GROWTH REGULATORS

The present invention concerns substituted 3,5-dioxo-3,4,5,6-tetrahydrooxazines as herbicides, processes and intermediates for their preparation, compositions containing them and their use as herbicides and acaricides.

More particularly, the invention concerns compounds of formula I

wherein

A represents the group (i)



(i)

in which any free hydrogen may be replaced by an agriculturally acceptable substituent; and B represents an optionally substituted aryl or heteroaryl group.

Examples of such B groups include phenyl, furyl, thienyl, pyrrolyl, pyrazolyl, imidazoyl, triazolyl, dithiolyl, oxathiolyl, isoxazolyl, oxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, oxatriazolyl, dioxazolyl, oxathiazolyl, dioxinyl, pyridazinyl, pyrazinyl, triazinyl, oxazinyl, isoxazinyl, oxathiazinyl, morpholinyl, azepinyl, oxepinyl, thiepinyl, diazepinyl, benzofuranyl, isobenzofuranyl, benzothienyl, isobenzothienyl, thionaphthalenyl, isothionaphthalenyl, indolyl, isoindolyl, indazolyl, indoleninyl, isobenzazolyl, pyranopyrrolyl, isoindazolyl, indoxazinyl, benzoxazolyl, benzopyranyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinoxalinyl, quinazolinyl, naphthyridinyl, pyridopyridinyl, pyranyl, thiapyranyl, chromenyl, thiachromenyl, benzoxazinyl, benzisoxazinyl and purine.

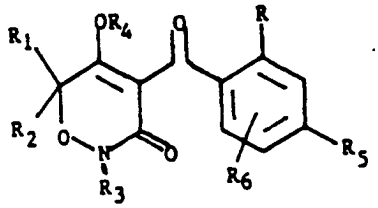
Examples of substitutents which may be present on ring (i) include alkyl, carboxy, alkoxycarbonyl and phenyl, itself optionally substituted, or a spiro-ring. The hydroxy group may be substituted e.g. by alkyl, alkylcarbonyl, optionally substituted arylcarbonyl, alkoxycarbonyl, aminocarbonyl (optionally substituted), alkylsulphonyl, phosphonyl (optionally substituted) phosphinyl (optionally substituted) or may form salts.

Examples of substituents which may be present on B include one or more alkyl, haloalkyl, alkoxy, haloalkoxy, halogen, nitro, cyano, alkyl $S(O)_n'$, haloalkyl $S(O)_n'$, cyanoalkyl $S(O)_n'$, alkylsulphonyloxy, haloalkylsulphonylamino (including mono and dialkylamino), phenyl $S(O)_n'$, benzyl $S(O)_n'$, amino, alkylamino, dialkylamino, alkylcarbonyl, alkoxycarbonyl, aminosulphonyl, alkylaminosulphonyl, dialkylaminosulphonyl, alkylcarbonylamino, alkylcarbonylalkylamino, formylamino, formylalkylamino groups. n is 0, 1 or 2.

B is preferably phenyl, unsubstituted or substituted, as mentioned above.

USP 4,695,673 describes a wide range of acylated 1,3-dicarbonyl compounds and their use as herbicides but makes no reference to or suggestion of the 3,5-dioxotetrahydrooxazine ring characterizing the compounds of the present invention.

A particular group of compounds of formula I is comprised of those of formula Ia



Ia

wherein each of R_1, R_2 and R_3 is independently hydrogen, C_{1-8}alkyl, carboxyl, C_{1-4}alkoxycarbonyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R, or R_1 and R_2

together form a C_{2-6}alkylene bridge;
R_4 is hydrogen, C_{1-8}alkyl, C_{1-8}alkylcarbonyl, C_{1-8}alkoxycarbonyl, $C(O)NR_7R_8$, C_{1-8}alkylsulphonyl, $P(O)(OR_9)(OR_9')$, $R_7P(O)\text{-}OR_9$, benzoyl or a cation;
R is C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms, C_{1-8}alkoxy optionally substituted by 1 to 6 halogen atoms, C_{1-8}alkylcarbonyl, C_{1-8}alkoxycarbonyl, $NR_7'R_8'$, $O_nS(O)_n'R_{10}$, $NR_7'SO_2R_8'$, halogen, cyano or nitro;
each of R_5 and R_6 is independently hydrogen or selected from the meanings given for R; or
R_5 and R_6 together form the group -Y-W-Z- with the proviso that R_5 and R_6 attach to adjacent carbon atoms of the phenyl ring of the compound of formula Ia;
each of R_7, R_7', R_7'', R_8, R_8' and R_8'' is independently hydrogen or C_{1-8}alkyl;
each of R_9 and R_9' are independently C_{1-8}alkyl;
R_{10} is C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms;
each of R_{11}, R_{12}, R_{13} and R_{14} is independently hydrogen, halogen or C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms;
W is $-(CR_{11}R_{12})_t\text{-}(CR_{13}R_{14})_t'$- or sulphonyl;
each of Y and Z is independently oxygen, sulphur, sulphonyl, $CR_7''R_8''$;
n is 0 or 1;
n' is 0, 1 or 2;
t is 1 or 2; and
t' is 0 or 1.

In the above definitions, halogen is conveniently selected from chloro, bromo and fluoro, C_{1-8}alkyl moieties, preferably have 1 to 4 carbon atoms.

Each of R_1, R_2 and R_3 is preferably hydrogen, C_{1-4}alkyl especially hydrogen or C_{1-3}alkyl. Where R_1 and R_2 together form an alkylene bridge, it is preferably a C_{3-6}alkylene bridge.

R conveniently signifies C_{1-4}alkyl optionally substituted with halogen, $-(O)_n\text{-}S(O)_n'\text{-}C_{1-4}$alkyl, halogen or nitro. It is preferably methyl, CF_3, C_{1-3}alkylsulfonyl, C_{1-3}alkylsulfonyloxy, chloro, bromo or nitro.

R_5 is preferably bromo, chloro, fluoro, trifluoromethyl, SC_{1-4}alkyl, OSO_2C_{1-4}alkyl, SO_2C_{1-4}alkyl, OSO_2C_{1-4}haloalkyl, $NR_7'SO_2C_{1-4}$alkyl, or, together with R_6, the group -Y-W-Z-. It is more preferably chloro, C_{1-3}alkylsulfonyl or C_{1-3}alkylsulfonyloxy, or, together with R_6, methylenedioxy.

R_6 is preferably hydrogen, C_{1-4}alkyl, C_{1-4}alkoxy, bromo, chloro or, together with R_5, the group -Y-W-Z-; it is more preferably hydrogen, methoxy or chloro, or, together with R_5, methylenedioxy.

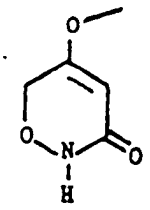
R_4 is conveniently hydrogen, C_{1-4}alkyl, C_{4-6}alkylcarbonyl, benzoyl, C_{1-4}alkylsulfonyl or a cation. It is preferably hydrogen, methyl, ethyl, t-butylcarbonyl, isobutylcarbonyl, benzoyl or methylsulfonyl. As a cation R_4 is preferably an alkali metal such as Na^+, K^+, Li^+ or an ammonium cation.

R_1 and R_2 are preferably H, C_{1-4}alkyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R; more preferably H or C_{1-3}alkyl e.g. H and methyl;
R_3 is preferably C_{1-8}alkyl, more preferably C_{1-4}alkyl, e.g., CH_3 C_2H_5;
R_4 is preferably H;
R_1 is preferably NO_2, Cl, CF_3, more preferably NO_2 or Cl;
R_5 is preferably Cl, Br, F, CF_3, $SO_2\text{-}R_{10}$, SR_{10}, OSO_2R_{10}, more preferably Cl, CF_3, OSO_2R_{10}, or SR_{10}, e.g., Cl, CF_3 or SCH_3;
R_6 is preferably H;
R_{10} is preferably C_{1-4}alkyl optionally halogen substituted, more preferably C_{1-3}alkyl optionally halogen substituted, e.g., C_{1-3}alkyl.

Preferred groups (i) are those in which R_1, R_2 and R_3 are each methyl and R_4 is hydrogen. Preferred groups B are those in which R_6 is hydrogen, R is nitro and R_5 is chloro or SCH_3. Two particularly preferred compounds are 2,6,6-trimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione, and 2,6,6-trimethyl-4-(4-methylthio-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H, 6H)-dione.

The compounds of the present invention of formula I are new substances which can be prepared by methods analogous to methods known in the art for the preparation of 2-aroyl-1,3-cycloalkyl-1,3-diones. More particularly, they can be obtained by, for example: rearranging an enol ester of formula (II)

wherein A' represents the group (ii)



(ii)

in which any free hydrogen may be replaced by an agriculturally acceptable substituent and B is as defined above to give a compound wherein the OH group in group (i) is unsubstituted (e.g. R_4 is H in compounds Ia).

This rearrangement is conveniently effected by reacting the compound of formula II with a cyanide source and a moderate base.

For example, the reaction may be carried out in the presence of a catalytic amount of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base. The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. 1,2-dichloroethane, toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide (DMF) and methyl isobutyl ketone (MIBK). In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 80 °C. In some cases, for instance when there is a possible problem of excessive by-product formation, the temperatures should be kept at about 40 °C maximum.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C_2-C_5 aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin. The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. Generally about 1-10 mol % of the cyanide source is preferred.

By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this reaction include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate. The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 1.3-2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly, potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

Compounds of formula I where the OH group in the group (i) is substituted can be prepared by reacting a compound of formula I wherein the OH group in the group (i) is unsubstituted with either

a) the group R_{40}-OH and a catalyst, or

b) the group R_{40}-Q and a moderate base, wherein Q is a halogen atom, to give a compound of formula I where R_{40} is the desired substituent, e.g., one of the substituents defined for R_4 but excluding hydrogen.

The above reaction a) is carried out in the presence of a catalyst such as concentrated sulfuric acid. The reaction is conveniently carried out in a solvent which is also the reactant such as methanol, and at an elevated temperature.

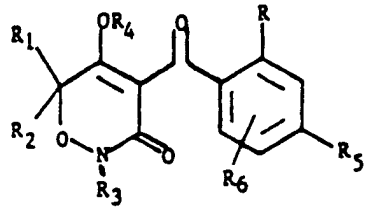
The above reaction b) is carried out in the presence of a moderate base such as triethylamine or pyridine and conveniently at RT or below.

The salt forms of compounds of formula I may be prepared by methods known per se, for example by reacting stoichiometric quantities of the compounds of formula I wherein R_4 is hydrogen with an appropriate base, for example, an alkali metal hydroxide, carbonate or bicarbonate, an alkaline earth metal hydroxide or carbonate, ammonia or an amine (e.g. diethanolamine, triethanolamine, octylamine, morpholine or dioctylamine), in a suitable solvent. Acid addition salts of compounds of general formula I which incorporate an amino radical may be prepared from the corresponding compounds of formula I by methods known per se, for example by reacting stoichiometric quantities of the compound of formula I and the appropriate acid, for example an inorganic acid, e.g. hydrochloric acid, sulphuric acid, phosphoric acid or nitric acid, or an

organic acid, e.g. acetic acid, in a suitable solvent. The salts may, if necessary, be purified by recrystallisation from one, two or more suitable solvents.

The compounds of formula I may be recovered from the reaction mixture in which they are formed by working up by established procedures.

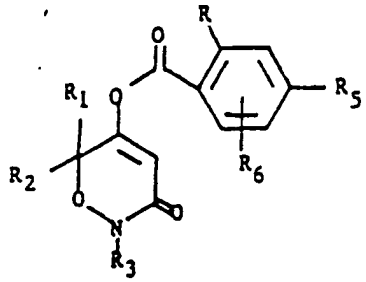
Under analogous conditions as described above, the compounds of the formula Ia



Ia

wherein R-R_3, R_5 and R_6 re as previously defined may be prepared by

a) when R_4 is H, rearranging an enol ester of formula IIa



IIa

wherein R-R_3, R_5 and R_6 are as previously defined;or

b) when R_4 is as previously defined but excluding H, reacting a compound of formula Ia wherein R_4 is H and R-R_3, R_5 and R_6 are as previously defined with either

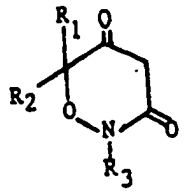
i) the group R_4-OH and a catalyst, or

ii) the group R_4-Q and a moderate base, wherein Q is a halogen atom; and

R_4 is as previously defined but excluding H.

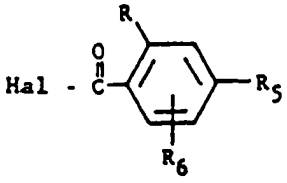
Similarly, the salt forms of compounds of formula Ia may be prepared according to the procedure described above for preparing the salt forms of the compounds of formlula I.

The compounds of formula IIa may be prepared by reacting a compound of formula III



III

with a compound of formula IV



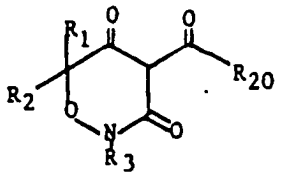
IV

This reaction is carried out in the presence of a base such as triethylamine, potassium carbonate, pyridine, preferably triethylamine and in an inert solvent such as dichloromethane, acetonitrile, toluene, tetrahydrofuran, dimethylformamide. The reaction is conveniently carried out at RT or below.

The remaining compounds of formula II may be prepared analogously.

The compounds of formula III are new and also form part of the invention.

They may be prepared by decarboxylating a compound of formula V



V

wherein R_{20} is alkoxy, especially ethoxy or methoxy and R_1, R_2 and R_3 are as defined above. The reaction may be carried out at elevated temperatures e.g. 80-90° and in an inert solvent such as e.g. wet dimethylsulfoxide.

The compounds of formula V may be prepared analogously to known methods e.g. according to the following reaction scheme.

$$R_3NHOC(R_1R_2)COOR_{20} \quad (VI) \quad + \quad ClOCCH_2COOR_{20} \quad (VII) \quad \xrightarrow{(a)}$$

$$R_3NOC(R_1R_2)COOR_{20}$$
$$COCH_2COOR_{20} \quad (VIII) \quad \xrightarrow{(b)} \quad V$$

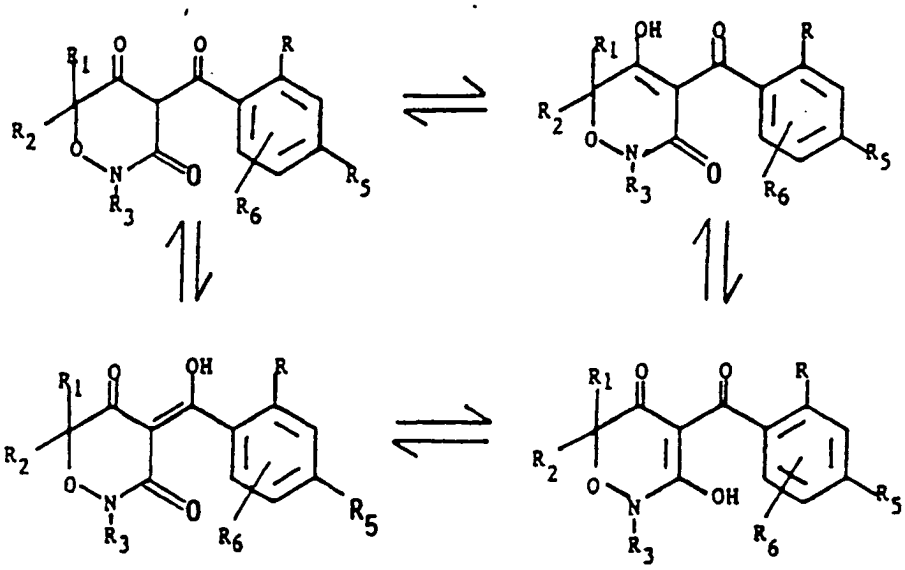
wherein R_{1-3} and R_{20} are as previously defined.

Reaction (a) may be carried out in an inert solvent such as dichloromethane and aqueous ether and in the presence of a base such as triethylamine or sodium carbonate at RT.

Reaction (b) may be carried out in an inert solvent such as toluene benzene or tetrahydrofuran in the presence of a base such as sodium methoxide or sodium hydride.

The remaining starting materials and reagents employed in the process described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the processes described herein or to known processes [cf for compounds VI Kornowski et al. Bull. Soc. Chim France 1966(2)683].

The compounds of this invention wherein the OH group in group (i) is unsubstituted can have four structural formulae because of tautomerism as illustrated as follows for formula Ia where R_4 is H:



The novel compounds of formula I are useful for the control of weeds, using pre- and/or post-emergent treatments. Compounds of formula I are also useful as plant growth regulators (PGRs) and acaricides. The compounds can be applied in the form of dusts, granules, solutions, emulsions, wettable powders, flowables and suspensions. Application of a compound of the present invention as herbicides is made according to conventional procedure to the weeds or their locus using an herbicidally effective amount of the compounds, usually from about one-tenth or less to ten pounds per acre (0.11 or less to 11 kg/ha, e.g. 0.05 to 11 kg/ha) more usually 0.05 to 5 kg/ha, and preferably 0.1 to 1 kg/ha, the application being repeated as necessary. The application of a compound of the present invention to the "locus" of the weed includes application to the seeds, the plant (weed) or parts of the plant, or the soil.

Application of a compound of the present invention as an acaracide is made according to conventional procedure to the site of infestation using an acaricidally effective amount of the compound, usually 100 g/ha to 1 kg/ha.

The term "herbicide", as used herein, refers to an active ingredient which modifies the growth of plants because of phytotoxic or plant growth regulating properties so as to retard the growth of the plant or damage the plant sufficiently to kill it.

The compounds of the present invention, when applied as either post or pre-emergents, demonstrate high levels of herbicidal activity on broadleaf, grass and sedge weeds. They also exhibit selectivity in wheat (e.g. compound 6 in Table A); corn and cotton (e.g. compound 2 in Table A); and rice.

In the use of the compounds of formula I for combatting weeds and acari, a compound of formula I, or mixture thereof, can conveniently be employed as compositions in association with acceptable diluent(s) for application to the weed, acari or their loci: such compositions also form part of the present invention.

Methods of preparing suitable formulations which can be used with a compound of the present invention are described in the literature along with suitable liquid or solid carriers. The optimum usage of a compound of the present invention is readily determinable by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot testing.

Suitable formulations contain from 0.01 to 99 % by weight of active ingredient, from 0 to 20 % of surfactant and from 1 to 99.99 % of solid or liquid diluent(s). Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms a composition generally contain between 0.01 and 25 % by weight of active ingredient. Lower of higher levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90 %, preferably between 5 and 80 % by weight of active ingredient.

Useful formulations of the compounds of formula I include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula I with the diluent(s) and optionally with other ingredients.

Alternatively, the compounds of formula I may be used in micro-encapsulated form.

The compounds of formula I can be combined with a cylcodextrin to make a cylcodextrin inclusion complex for application to the weeds, acari or their loci.

Agriculturally acceptable additives may be employed in the herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such xylene or an alcohol such as isopropanol, and for liquid application forms, e.g. water or diesel oil.

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary acaricidal or herbicidal activity for broadspectrum weed control or compounds having antidotal, fungicidal, insecticidal or insect attractant activity.

Typical herbicidal composition, according to this invention, are illustrated by the following Examples A, B and C in which the quantities are in parts by weight.

EXAMPLE A

Preparation of a Dust

10 Parts of a compound according to this invention and 90 parts of powdered talc are mixed in a mechanical grinder-blender and are ground until a homogeneous, free-flowing dust of the desired particle size is obtained. This dust is suitable for direct application to the site of the weed infestation.

EXAMPLE B

Preparation of Wettable Powder

25 Parts of a compound according to this invention are mixed and milled with 25 parts of synthetic fine silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium ligninsulphonate and 45 parts of finely divided kaolin until the mean particle size is about 5 micron. The resulting wettable powder is diluted with water before use to a spray liquor with the desired concentration.

EXAMPLE C

Preparation of Emulsifiable Concentrates (EC)

13.37 Parts of a compound according to this invention are mixed in a beaker with 1.43 parts of Toximul 360A (a mixture of anionic and non-ionic surfactants containing largely anionic surfactants), 5.61 parts of Toximul 360A (a mixture of anionic and non-ionic surfactants containing largely non-ionic surfactants), 23.79 parts of dimethyl formamide and 55.8 parts of Tenneco 500-100 (predominantly a mixture of alkylated aromatics such as xylene and ethylbenzene) until solution is effected. The resulting EC is diluted with water for use.

The following Examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight.

FINAL COMPOUNDS

EXAMPLE I

Preparation of 2,6-dimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione (formula Ia wherein R_1 and R_3 are CH_3; R_2, R_4 and R_6 are H; R is NO_2; R_5 is Cl; (Compound No. 1 Table A)).

3.65 g of 2,6-dimethyl-5-(4-chloro-2-nitrobenzoyloxy)-6H-1,2-oxazine-3-one is treated at r.t. with 3.06 ml of triethylamine and 0.3 ml of acetone cyanohydrin in 20 ml of acetonitrile (20 ml). After stirring overnight the solution is concentrated to a small volume and then taken up in dichloromethane and water. The combined extracts are washed with dilute HCl, brine, dried and evaporated to yield an oily residue. The crude product is recrystallized from ether to give crystalline 2,6-dimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione, M.P. 127.5° C.

Proceeding analogously to Example Ia the following compounds of formula I are obtained.

TABLE A

Cpd	R_1	R_2	R_3	R_4	R	R_5	R_6	m.p.
1	CH_3	H	CH_3	H	NO_2	4-Cl	H	127.5°
2	CH_3	CH_3	CH_3	H	NO_2	4-Cl	H	105°
3	CH_3	CH_3	CH_3	H	Cl	4-SO_2CH_3	H	110°
4	CH_3	CH_3	CH_3	H	NO_2	4-Br	H	Foam
5	CH_3	CH_3	CH_3	H	NO_2	4-OSO_2CH_3	H	128°
6	CH_3	CH_3	CH_3	H	NO_2	4-SCH_3	H	104-6°
7	CH_3	CH_3	CH_3	H	NO_2	4-F	H	137°
8	CH_3	CH_3	CH_3	H	NO_2	4-SO_2CH_3	H	124°
9	CH_3	CH_3	C_2H_5	H	NO_2	4-Cl	H	Foam
10	CH_3	CH_3	C_2H_5	H	NO_2	4-OSO_2CH_3	H	115°
11	CH_3	CH_3	CH_3	H	CF_3	4-F	H	86°
12	CH_3	CH_3	CH_3	H	NO_2	4-CF_3	H	102-103.5°
13	CH_3	CH_3	CH_3	H	NO_2	4-SO_2CH_2Cl	H	
14	CH_3	CH_3	CH_3	H	NO_2	4-$SO_2C_2H_5$	H	
15	H	H	C_2H_5	H	NO_2	4-Cl	H	
16	H	H	n-C_3H_7	H	NO_2	4-Cl	H	
17	H	H	n-C_4H_9	H	NO_2	4-Cl	H	
18	H	H	n-C_4H_9	H	NO_2	4-CF_3	H	
19	CH_3	H	n-C_3H_7	H	NO_2	4-Cl	H	
20	CH_3	H	n-C_3H_7	H	NO_2	4-CF_3	H	
21	CH_3	CH_3	CH_3	H	NO_2	H	H	87.5°
22	CH_3	CH_3	CH_3	H	NO_2	$OCHF_2$	H	

NMR Spectra

Compound 4

^{1}H nmr ($CDCL_3$): δ 1.30, 1.53 (s,s,6H,$C(CH_3)_2$), 3.08, 3.38 (s,s,3H,NCH_3) 7.21 (d,1H,8Hz), 7.83 (dd,1H,8Hz), 8.33 (d,1H,2Hz-phenyl H)

Compound 9

^{1}H nmr ($CDCL_3$): δ 1.33, 1.53 (s,s,6H,$C(CH_3)_2$), 1.20 (m, 3H,$NCH_2\underline{C}H_3$), 3.66 (m,2H,$NC\underline{H}_2CH_3$), 7.28 (d,1H,8Hz), 7.66 (dd,1H,8Hz), 8.18 (d,1H,2Hz-phenyl H).

EXAMPLE 2

Preparation of 2,6-dimethyl-5-(4-chloro-2-nitrobenzoyloxy)-6H-1,2-oxazine-3-one (formula IIa, $R_1 = R_3 = CH_3$, $R_2 = R_6 = H$, $R = NO_2$, $R_5 = Cl$)

To a solution of 1.77 g of 2,6-dimethyl-2H-1,2-oxazine-3,4(4H,6H)-dione in 15 ml of dichloromethane containing 2.4 ml of triethylamine is added dropwise at 0° C solution of 2.72 g of 4-chloro-2-nitrobenzoyl chloride in 10 ml of dichloromethane. After the addition is complete, the reaction mixture is stirred at r.t. for one hour, then diluted with dichloromethane, washed, dried and evaporated to dryness to give the title compound.

EXAMPLE 3

Preparation of 2,6-dimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione (Formula III $R_1 = R_3 = CH_3$, $R_2 = H$)

4.9 g of an oily mixture of 2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione and 2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione is obtained e.g. as illustrated below is heated at 79° C in 25 ml of DMSO and 0.9 ml of water for 3 hours. The reaction mixture is taken up in ether, poured into water and extracted thoroughly with ether. The combined extracts are dried and evaporated to give 2,6-dimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione.

The following two diones may be prepared analogously.

2,6,6-trimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione (Formula III $R_1 = R_2 = R_3 = CH_3$)

2-ethyl-6,6-dimethyl-2H-1,2-oxazine-3,5-(4H,6H)-dione (Formula III $R_1 = R_2 = CH_3$, $R_3 = C_2H_5$).

EXAMPLE 4

Preparation of 2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione and 2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione as a mixture.

To a suspended solution of sodium methoxide, freshly prepared from 694 mg of sodium metal and methanol, in 45 ml of toluene is added dropwise at r.t. a solution of 7.1 g of methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate, in 10 ml of toluene. After completing the addition, the resulting mixture is stirred at r.t. for 24 hours. The reaction mixture is poured into ice-water and extracted with ether (discarded). The aqueous solution is then acidified with 10% aqueous HCL and extracted with dichloromethane. The combined extracts were dried and evaporated to dryness to yield an oily mixture of the title compounds.

EXAMPLE 5

Preparation of methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate

To a solution of 5.32 g of methyl 2-methylaminooxypropionate in 50 ml of dichloromethane is added dropwise at 0° C a solution of 6.62 g of ethylmalonyl chloride in 15 ml of dichloromethane. After the addition is complete, the resulting solution is stirred at 0° C for additional one hour. The reaction mixture is poured into water, and extracted with ether. The combined extracts are washed with dilute HCL, brine, dried and evaporated to give an oily residue which is chromatographed on silica gel to yield oily methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate.

NMR spectra for the compounds of examples 2 to 5.

Example 2

^1H nmr ($CDCL_3$): δ 1.47 (d,3H,OCH(CH_3)), 3.20 (s,3H,NCH_3), 4.81 (q,1H,OCH(CH_3)), 6.15 (s,1H, = CHCO) and 7.77, 7.97 (s,dd,3H,phenyl H).

Example 3

^1H nmr ($CDCL_3$): δ 1.43 (d,3H,OCH(CH_3)), 3.30 (s,1H,NCH_3), 3.53 (q,2H,$OCCH_2CO$) and 4.40 (q,1H,OCH_3)).

Example 4

2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione

^{1}H nmr ($CDCL_3$): δ 1.50 (d,3H,OCH($\underline{CH_3}$)), 3.21 (s,3H,NCH_3), 3.93 (2,3H,OCH_3), and 4.73 (q,1H,OC$\underline{H}$-(CH_3)).

2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione

^{1}H nmr ($CDCL_3$): δ 1.40 (t,3H,$OCH_2\underline{CH_3}$), 1.48 (d,3H,OCH($\underline{CH_3}$)), 3.21 (s,3H,NCH_3), 4.41 (q,2H,$OC\underline{H_3}CH_3$) and 4.73 (q,1H,OC$\underline{H}$(CH_3)).

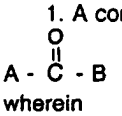
Example 5

Methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate

^{1}H nmr ($CDCL_3$): δ 1.28 (t,3H,$OCH_2\underline{CH_3}$), 3.23 (s,3H,NCH_3), 3.70 (q,2H,$OCCH_2CO$), 3.77 (s,3H,$0CH_3$), 4.21 (q,2H,$OC\underline{H_2}CH_3$) and 4.57 (q,1H,OC$\underline{H}$(CH_3).

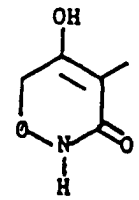
Claims

1. A compound of formula I



A - C - B I

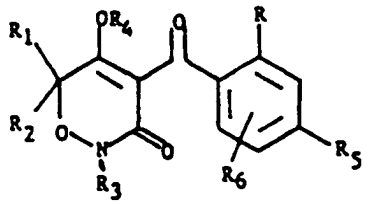
wherein
A represents the group (i)



(i)

in which any free hydrogen may be replaced by an agriculturally acceptable substituent; and B represents an optionally substituted aryl or heteroaryl group.

2. A compound having the formula Ia



Ia

wherein each of R_1, R_2 and R_3 is independently hydrogen, C_{1-8}alkyl, carboxyl, C_{1-4}alkoxycarbonyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R, or R_1 and R_2 together form a C_{2-6}alkylene bridge;
R_4 is hydrogen, C_{1-8}alkyl, C_{1-8}alkylcarbonyl, C_{1-8}alkoxycarbonyl, $C(O)NR_7R_8$, C_{1-8}alkylsulphonyl, P(O)-

$(OR_9)(OR_9')$, $R_7P(O)$-OR_9, benzoyl or a cation;
R is C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms, C_{1-8}alkoxy optionally substituted by 1 to 6 halogen atoms, C_{1-8}alkylcarbonyl, C_{1-8}alkoxycarbonyl, $NR_7'R_8'$, $O_nS(O)_n'R_{10}$, $NR_7'SO_2R_8'$, halogen, cyano or nitro;
each of R_5 and R_6 is independently hydrogen or selected from the meanings given for R; or
R_5 and R_6 together form the group -Y-W-Z- with the proviso that R_5 and R_6 attach to adjacent carbon atoms of the phenyl ring of the compound of formula Ia;
each of R_7, R_7', R_7'', R_8' R_8, and R_8'' is independently hydrogen or C_{1-8}alkyl;
each of R_9 and R_9' are independently C_{1-8}alkyl;
R_{10} is C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms;
each of R_{11}, R_{12}, R_{13} and R_{14} is independently hydrogen, halogen or C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms;
W is $-(CR_{11}R_{12})_t-(CR_{13}R_{14})_t'-$ or sulphonyl;
each of R_{13} and R_{14} is independently hydrogen, halogen or C_{1-8}alkyl optionally substituted by 1 to 6 halogen atoms;
n is 0 or 1;
n' is 0, 1 or 2;
t is 1 or 2; and
t' is 0 or 1.

3. A compound according to Claim 2, wherein
each of R_1, R_2, R_3 is independently selected from hydrogen or C_{1-4}alkyl;
R is selected from C_{1-4}alkyl optionally substituted with halogen, $-(O)_n-S(O)_n'C_{1-4}$alkyl, halogen or nitro;
R_5 is selected from bromo, chloro, SC_{1-4}alkyl, OSO_2C_{1-4}alkyl, SO_2C_{1-4}alkyl, OSO_2-C_{1-4}haloalkyl, $NR_7'SO_2C_{1-4}$alkyl, or, together with R_6 the group -Y-W-Z-;
R_6 is selected from hydrogen, C_{1-4}alkyl, C_{1-4}alkoxy, bromo, chloro or, together with R_5, the group -Y-W-Z-;
and R_4 is selected from H, C_{1-4}alkyl, C_{4-8}alkylcarbonyl, benzoyl, C_{1-4}alkylsulphonyl or a cation.

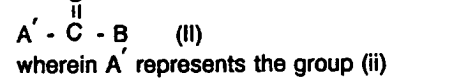
4. A compound according to Claim 2 wherein
each of R_1 and R_2 is independently selected from H, C_{1-4}alkyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R;
R_3 is C_{1-8}alkyl;
R_4 is H;
R is selected from NO_2 and Cl;
R_5 is selected from Cl, Br, F, SO_2R_{10}, SR_{10} and OSO_2R_{10};
R_6 is H;
and R_{10} is selected from C_{1-5}alkyl optionally halogen substituted.

5. A compound according to Claim 4, wherein R_1, R_2 and R_3 are each methyl, R_4 and R_6 are each hydrogen, R is nitro and R_5 is chloro or $-SCH_3$.

6. A pesticidal composition comprising the compound of formula I or Ia as defined in Claims 1 or 2 to 5, in association with an agriculturally acceptable carrier.

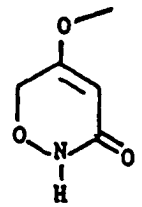
7. A method of controlling weeds comprising applying to the weeds or their locus a herbicidally effective amount of a compound of formula I or Ia as defined in Claims 1 or 2 to 5.

8. A process for preparing a compound of formula I as defined in Claim 1 which comprises
a) rearranging an enol ester of formula (II)



(II)

wherein A' represents the group (ii)



(ii)

in which any free hydrogen may be replaced by an agriculturally acceptable substituent and B is as defined

in Claim 1 to give a compound wherein the OH group in group (i) is unsubstituted;

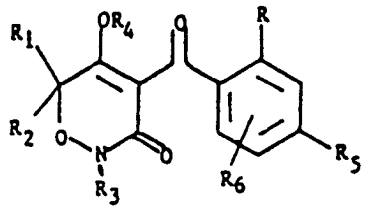
b) when the OH group in group (i) is substituted, reacting a compound of formula I wherein the OH group in the group (i) is unsubstituted with either

a) the group R_{40}-OH and a catalyst, or

b) the group R_{40}-Q and a moderate base, wherein Q is a halogen atom,

to give a compound of formula I where R_{40} is the desired substituent.

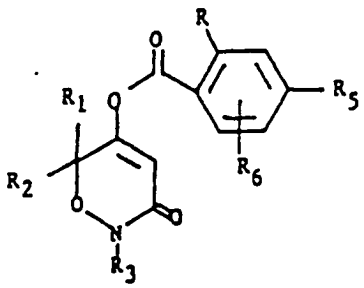
9. A process for preparing a compound of the formula Ia



Ia

wherein R-R_3, R_5 and R_6 are as defined in Claim 2, which comprises

a) when R_4 is H, rearranging an enol ester of formula IIa



IIa

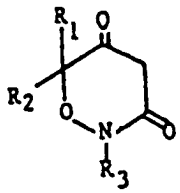
wherein R-R_3, R_5 and R_6 are as defined above; or

b) when R_4 is as defined in Claim 2 but excluding H, reacting a compound of formula Ia wherein R_4 is H and R-R_3, R_5 and R_6 are as defined in Claim 2 with either

i) the group R_4-OH and a catalyst, or

ii) the group R_4-Q and a moderate base, wherein Q is a halogen atom and R_4 is as defined in Claim 2 but excluding H.

10. A compound of formula III



III

wherein R_1, R_2 and R_3 are as defined in Claim 2.